Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic and Optical Properties of Polypyridylruthenium Derivatized Polystyrenes: Multi-level Computational Analysis of Metallo-Polymeric Chromophore Assemblies

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Supporting Information

SI1. INDO/S and DFT orbital pictures for selected monomer geometries from simulation.

SI1. INDO/S and DFT orbital pictures for gas-phase monomer geometries.

SI3. n0 pendant geometries showing *cis* and *trans* amide bonds.

SI4. Gaussian fitting to **n2** polymer HOMO distribution.

SI5. Plot of each monomer's contribution to the HOMO energy plot for **n0** polymer.

SI6. Plot of each monomer's contribution to the HOMO energy plot for **n1** polymer.

SI7. Plot of each monomer's contribution to the HOMO energy plot for **n2** polymer.

SI8. Plot of energy distributions for HOMO through HOMO-4 energies for **n0** polymer.

SI9. Plot of energy distributions for HOMO through HOMO-4 energies for **n1** polymer.

SI10. Plot of energy distributions for HOMO through HOMO-4 energies for **n2** polymer.

SI11. Orbital pictures for the $[Ru(Bpy)_3]^{2+}$, **n0**, **n1** and **n2** optimized monomers.

Fig. SI1. Comparing orbital pictures for selected monomers. All geometries were obtained from MD runs, and orbitals were calculated using both INDO/s (black and white) and DFT (color figures). It is clear that in both methods the orbitals are localized on the same atoms.

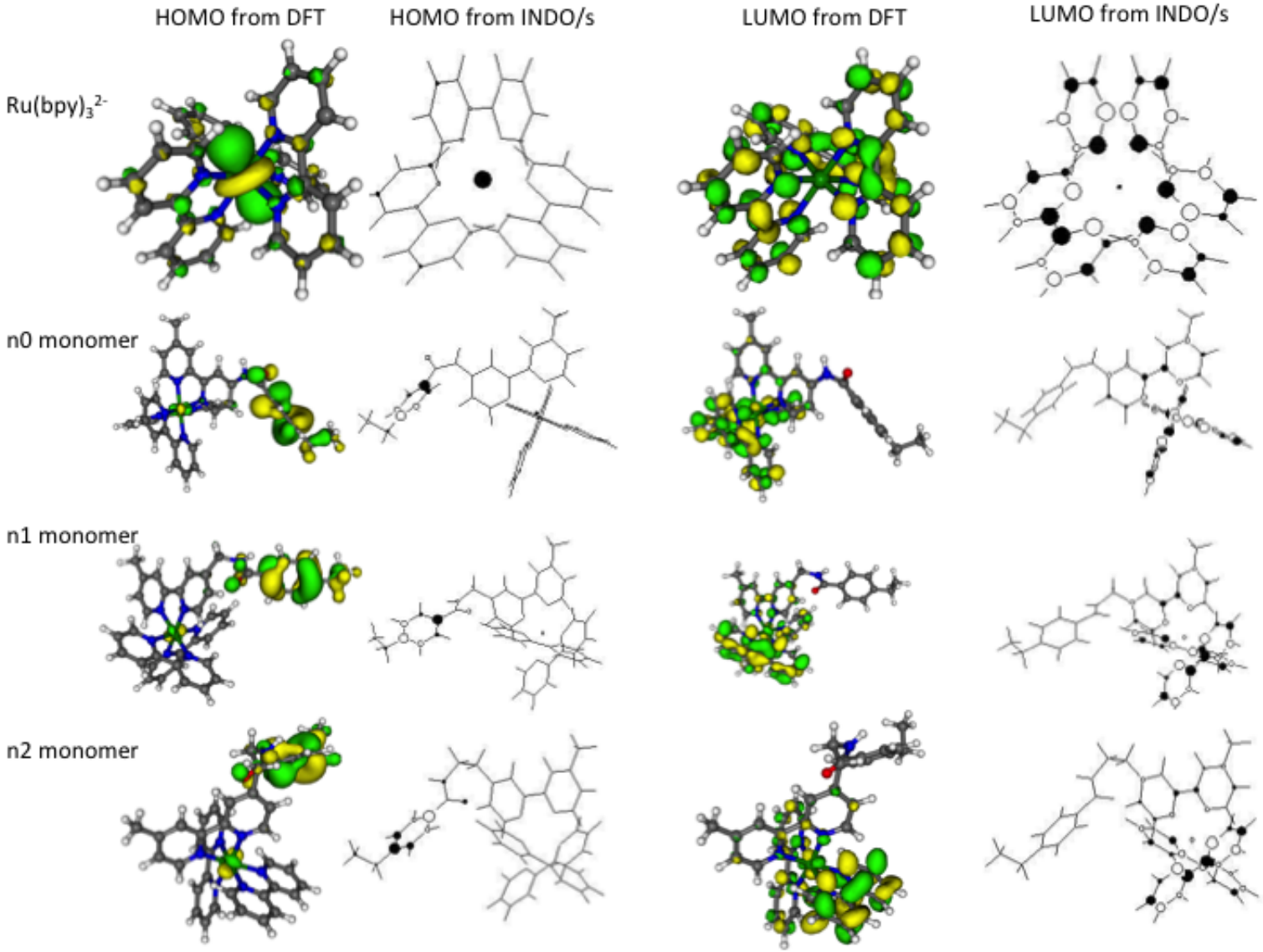

HOMO from DFT
HOMO from INDO/s
LUMO from DFT
LUMO from INDO/s
Ru(bpy)$_3^{2-}$
n0 monomer
n1 monomer
n2 monomer

Fig. SI2. Comparing orbital pictures for the $[Ru(Bpy)_3]^{2+}$, **n0**, **n1** and **n2** monomers. All geometries were optimized using DFT (B3LYP/Lanl2DZ) and the orbitals were calculated using DFT (same parameters as geometry optimization) or INDO/S. It is clear that in both methods the orbitals are localized on the same atoms. Note that the HOMO-LUMO gap in DFT is much smaller than in INDO/s (i.e. for $[Ru(Bpy)_3]^{2+}$: 3.4eV in DFT but 6.6eV in INDO/s).

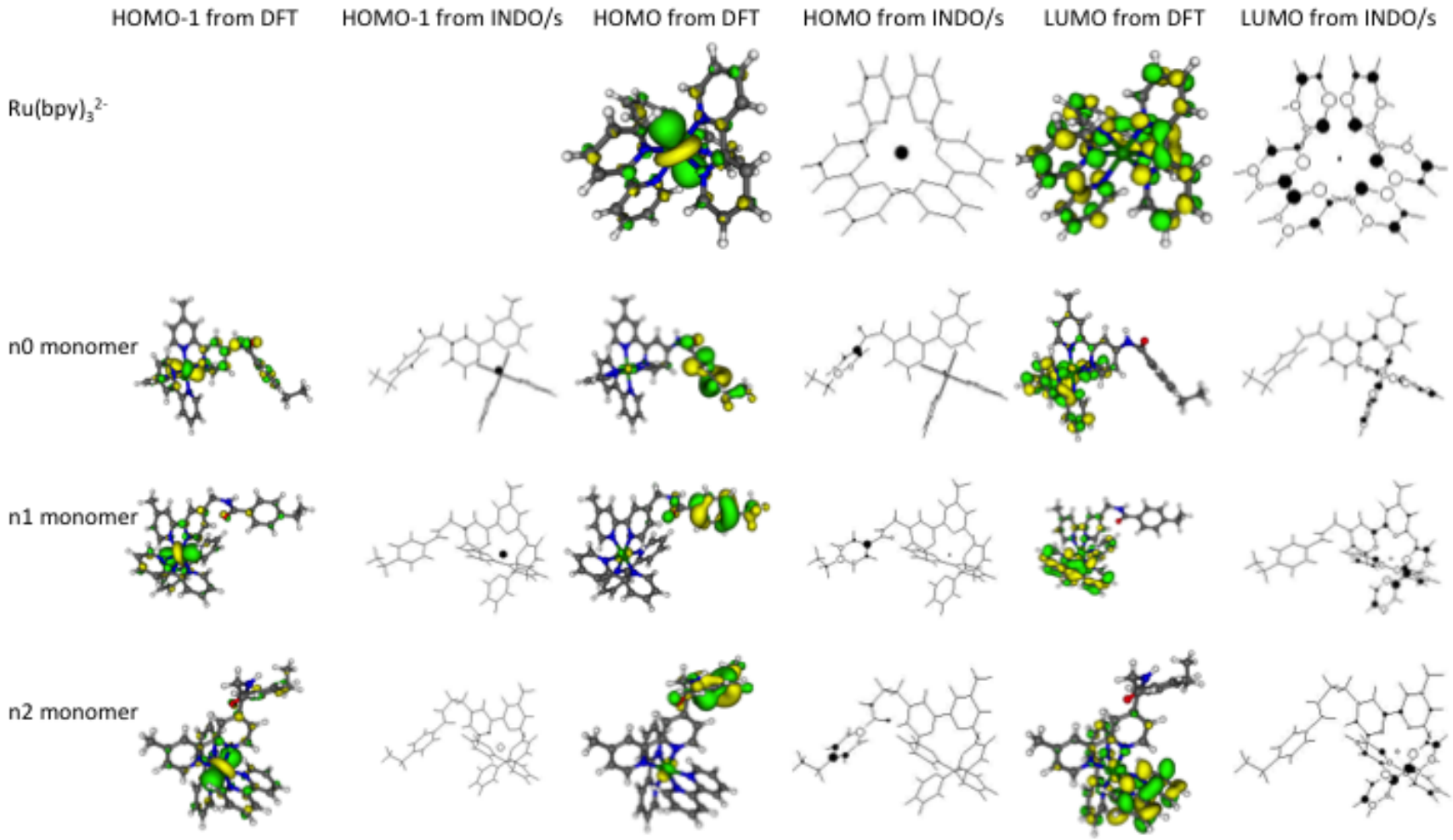


Fig. SI3. Selected geometries from the **n0** polymer, showing bimodal distribution.

A. amide bond is cis
B. amide bond is trans

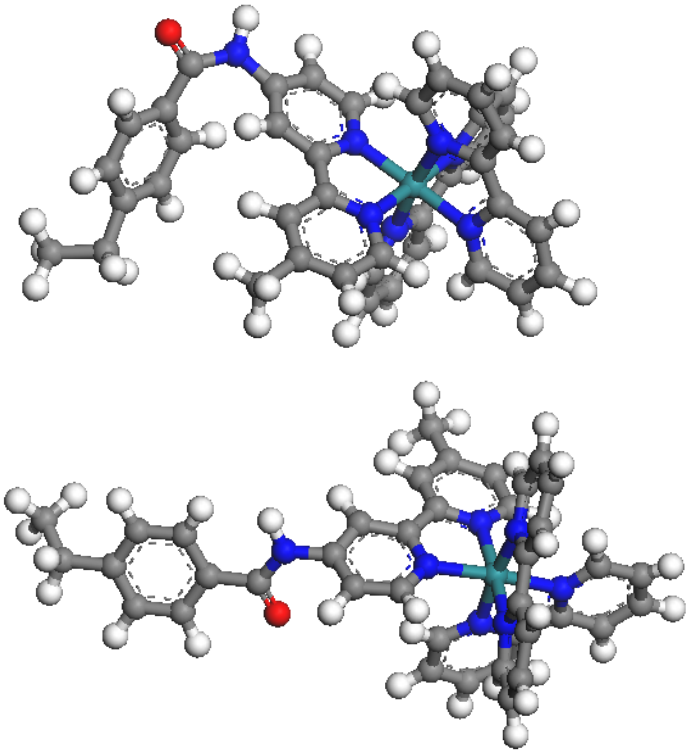


Fig. SI4. Energy distribution of HOMO orbitals from **n2**. The distribution can be fitted by 4 gaussians: g1 (mean = -12.7, halfwidth = 0.08, max height = 602); g2 (mean = -12.35, halfwidth = 0.21, max height = 369); g3 (mean= -11.8, halfwidth = 0.21, max height = 1753); and g4 (mean = -11.4, halfwidth = 0.17, max height = 3701).

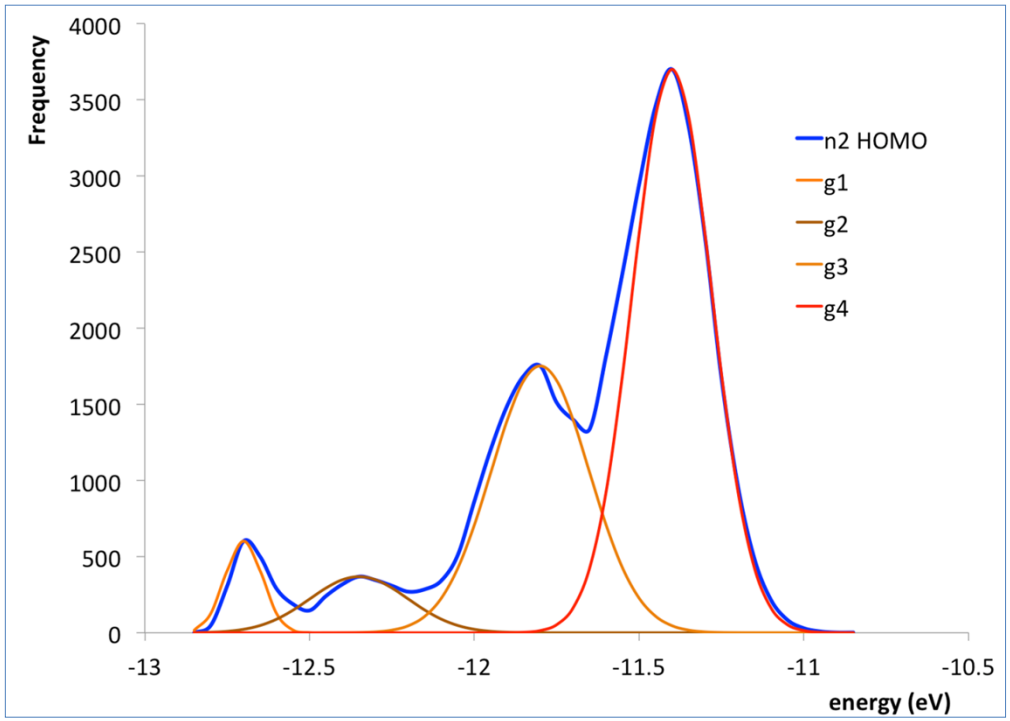


Fig. SI5. Plot of each monomer's contribution to the HOMO energy plot for **n0** polymer. The distributions are color-coded for each pendant in the polymer; the black line shows the scaled-down overall distribution.

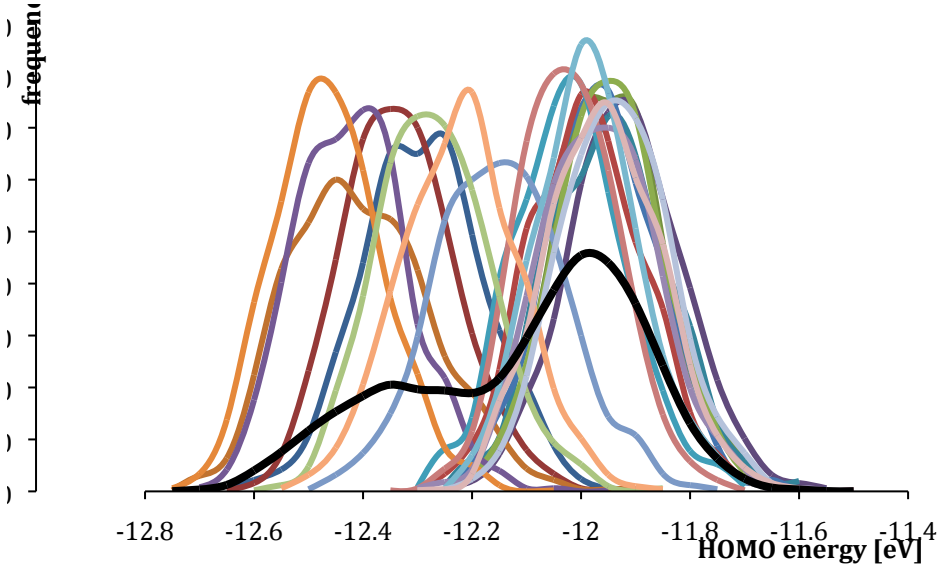


Fig. SI6. Plot of each monomer's contribution to the HOMO energy plot for **n1** polymer. The distributions are color-coded for each pendant in the polymer; the black line shows the scaled-down overall distribution.

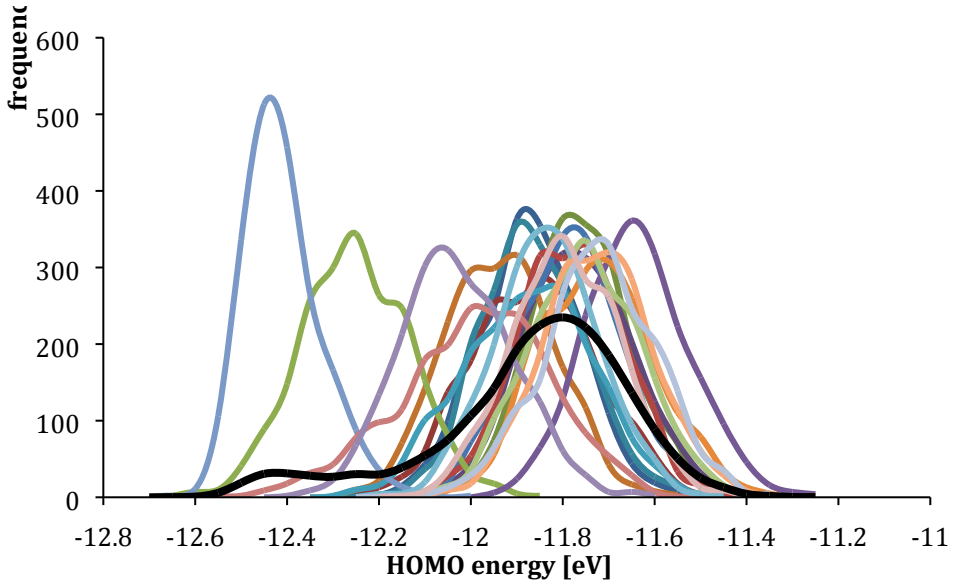
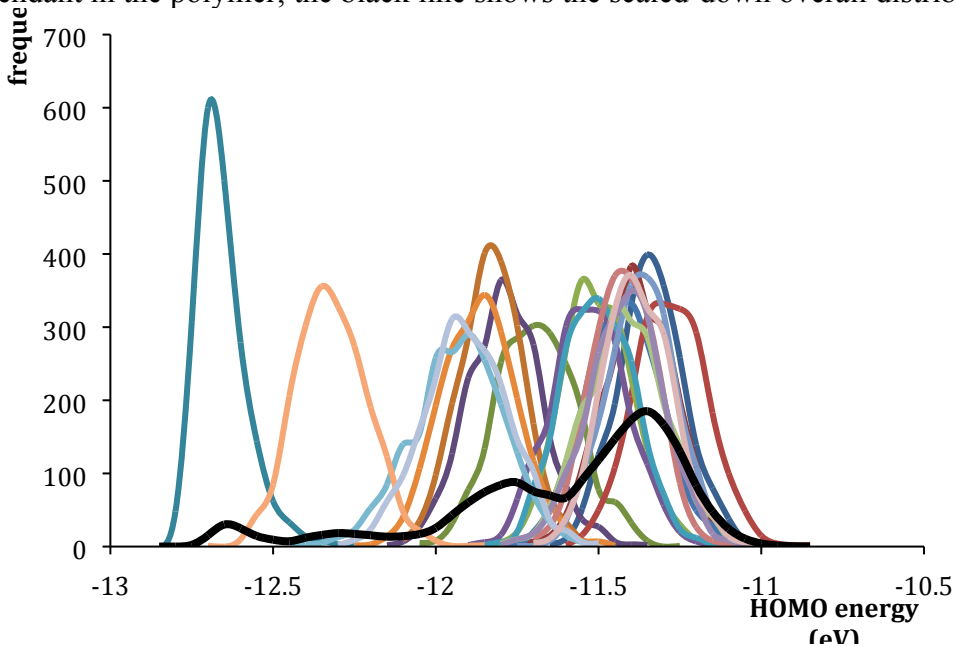
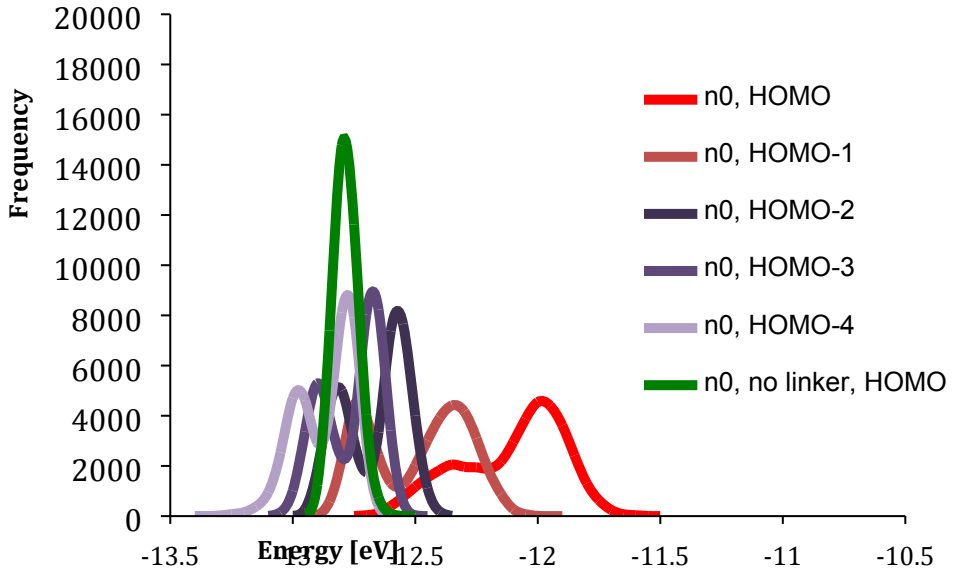


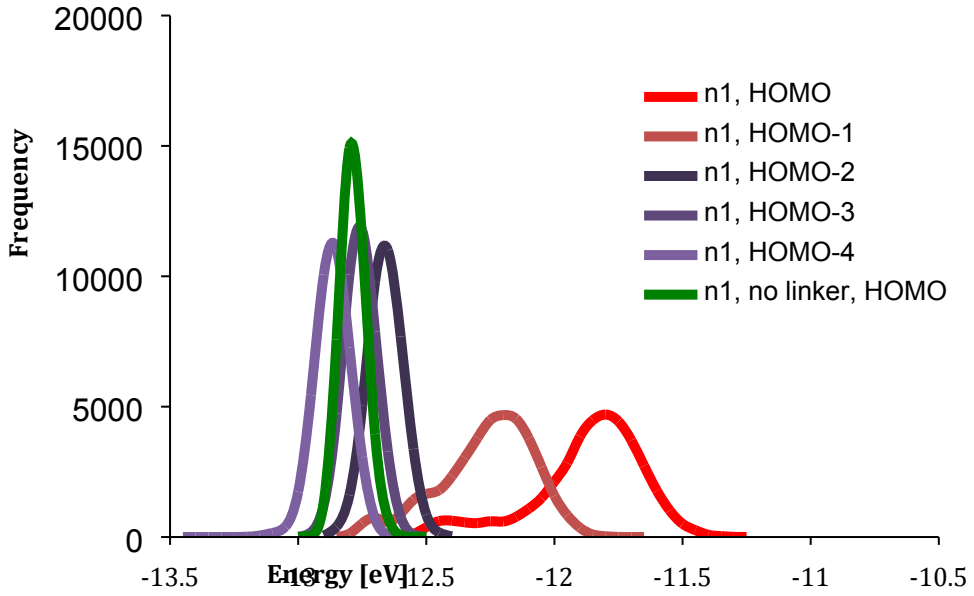
Fig. SI7. Plot of each monomer's contribution to the HOMO energy plot for **n2** polymer. The distributions are color-coded for each pendant in the polymer; the black line shows the scaled-down overall distribution.



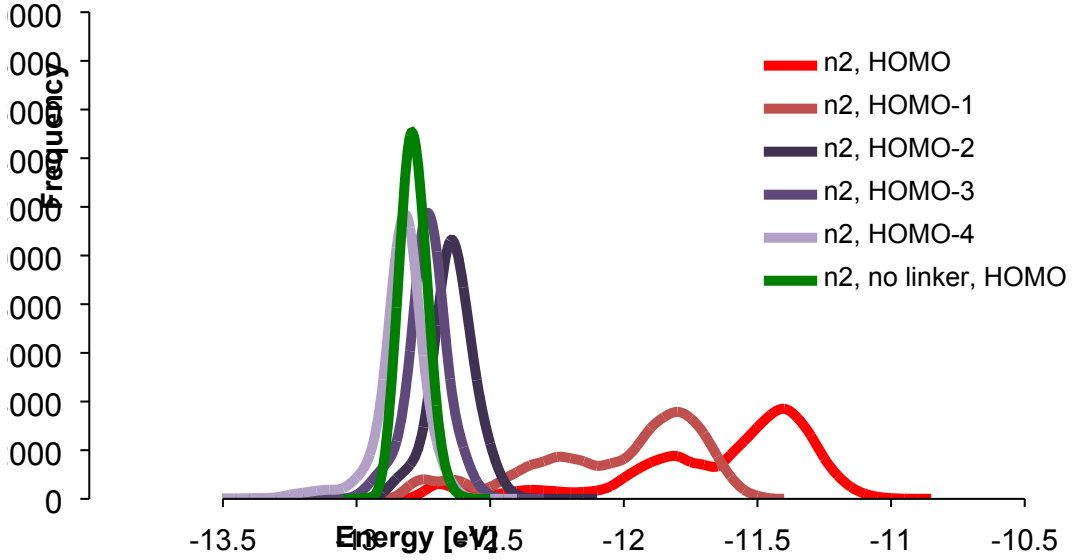
SI8. Plot of energy distributions for HOMO through HOMO-4 energies for **n0** polymer. The HOMO energy distribution for the pendants without linker is shown for comparison, in green.



SI9. Plot of energy distributions for HOMO through HOMO-4 energies for **n1** polymer. The HOMO energy distribution for the pendants without linker is shown for comparison, in green.



SI10. Plot of energy distributions for HOMO through HOMO-4 energies for **n2** polymer. The HOMO energy distribution for the pendants without linker is shown for comparison, in green.



SI11. Orbital pictures for the $[Ru(Bpy)_3]^{2+}$, **n0**, **n1** and **n2** optimized monomers. All geometries were optimized using DFT (B3LYP/Lanl2DZ) and the orbitals were calculated using DFT (same parameters as geometry optimization). H-2: HOMO-2, H-1: HOMO-1, H: HOMO, and L: LUMO